

*of T. M. Clarke
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PHOSPHATE CHEMISTRY

AS IT CONCERN THE MINER.

BY

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PHOSPHATE CHEMISTRY AS IT CONCERNNS THE MINER.

BY THOMAS M. CHATARD, WASHINGTON, D. C.

EVERY one engaged in the mining of phosphates is well aware that the price he gets for his product depends upon the results of chemical analysis. He knows that the value rises with the percentage of phosphoric acid, whether stated as such or as so-called "bone phosphate," and that deductions are made for certain constituents, such as alumina or oxide of iron, when the amount of these exceeds certain limits. The reason for these deductions is but vaguely understood by many, and there are few who possess the special knowledge required to form a competent judgment, either as to the reliability of the analysis on which so much depends, or as to how far and in what manner they may avail themselves of chemical investigation to aid them in improving the quality and quantity of their output.

The acquisition of this special knowledge is by no means easy, especially for the busy man who must pick it up as best he may and at odd times. So far as reading can aid, there are two books readily accessible. One is *The Nature and Origin of Deposits of Phosphate of Lime*, by R. A. F. Penrose, Jr., being Bulletin No. 46 of the United States Geological Survey, which, in addition to its own valuable matter, contains an extensive list of other publications on the subject. The other is the recently published *Phosphates of America*, by Dr. Francis Wyatt, which gives much information concerning the mining, preparation, manufacture, and analysis of phosphates. The remaining phosphate literature, though very extensive and rapidly increasing, is rarely in such shape as to be readily available to any one but the specialist. This is particularly the case with the descriptions of analytical methods, which are often vague even to the practiced chemist; and the proofs of the value of which are, in many cases, quite inadequate, while the vigor displayed in the attack and defence of views and methods is apt to confuse the non-professional reader. Nevertheless, whatever knowledge can be obtained from

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books will be found of value when the advice and assistance of the chemist is sought.

There are chemists and chemists; there are experts and pretenders; and if one has no previous knowledge of the subject, how can one distinguish between the two, and how can one weigh the value of advice or work. The greater the knowledge of the miners, the more frequent and exacting will be their demands on the chemists, who, in turn, will be stimulated and encouraged to make themselves—not what too many of them are, mere analysts, but what they ought to be—chemical engineers, having a practical knowledge and a clear comprehension of the principles and details of technical operations in the lines in which they profess to work. One hears much complaint among chemists that practical men are unwilling to pay a fair price for good work, and do not appreciate it when they get it. While this is unfortunately true in many instances, I cannot but think that it is, to a considerable extent, the fault of the chemists themselves. When called upon for advice as to the proper system and appliances for carrying out a given piece of practical work, how many of them are really capable of giving a reliable opinion based upon facts and figures of experience? They may be able scientific men; they may be accomplished analysts; but of industrial operations they have but the vaguest impressions, on which, too often, very extensive assertions are based. It cannot be too strongly insisted upon that those who desire to aid in the development of chemical industry should make themselves chemical engineers. There is the science of electricity; there is the profession of the electrical engineer; and it is hardly necessary to say that a man may be deeply learned in the sciences of geology, chemistry, mechanics, and heat, and yet have no claim to be considered a mining engineer. The chemical engineer, as distinguished from the mere analyst, must be able and ready not only to answer, through knowledge and investigation, the questions of his clients, but also to indicate to them new lines of progress. Such a man educates his clients; they, in turn, develop him; and only through such beneficial mutual reaction can we hope to reach that much to be desired time when, through a proper concert of action among miners and shippers of phosphate, as urged by Dr. Wyatt, uniformity in analytical methods and practice shall be enforced.

The present frequent occurrence of widely differing results between chemists working upon the same sample, can then, in great measure, be avoided, and the consequent vexations and expensive

disputes and lawsuits be prevented. The eighth chapter of Dr. Wyatt's book shows the advantages to be gained by such uniformity, and if all who are interested in establishing it will do their part, the arrival of the chemical millenium can be much hastened.

One of the obstacles is that there are different ways of determining each constituent of a phosphate. Each method has its defenders and opponents, and each chemist, if free to do so, will prefer to use his favorites, which, in his hands at least, yield results which satisfy him. Now, every one can readily understand that if two chemists, analyzing the same sample, use different methods, the results may, and probably will, vary widely. It is not so well known that, even when they use the same general methods, the results may differ decidedly if there are variations in the practical details of manipulation. The operative detail is very often the essence of a good method, and should, when published, be described at length, especially when intended for commercial analysis. No method should be adopted for the valuation of materials which has not already met with general favor after undergoing a searching ordeal of test and discussion; and a method once adopted should be carried out to the letter. Under such a system the honest, conscientious, painstaking worker will be appreciated.

The methods which have been used for the chemical work of the United States Geological Survey in Florida will be fully described at the end of this paper, so that they may be easily followed by others, and possible errors may be detected. None of them are original. I have preferred, for the reasons given above, to use such as have already attained a wide acceptance among chemists. Nor have any very important modifications been introduced, except in the determination of fluorine. If they are found to differ greatly from those advocated by some other chemists, they are offered in no spirit of contention or criticism, though it may be necessary, here and there, to point out these differences and their reasons. What we need are accurate standards, carefully described; and such I have tried to furnish. When the miner can see for himself what skill and labor are involved in the making of a trustworthy analysis, he ought to be willing to pay a fair price for good work.

The commercial valuation of a natural phosphate is based on an analysis showing a number of constituents, only one of which, the phosphoric acid, has any value. All the rest are either useless (like water and insoluble matter, which merely reduce the percentage of phosphoric acid) or hurtful (like carbonates, which, neutralizing

their equivalent of sulphuric acid, increase the cost of manufacture; or, like alumina and ferric oxide, which not only "revert" a portion of the "soluble" phosphoric acid, but also, in proportion to their amount, tend to render the superphosphate wet and unmanageable). Moreover, the amount of fluorine may be of great importance, since there are silicates of alumina which, otherwise unattacked by the sulphuric acid, are decomposed in the presence of fluorine, the otherwise inactive alumina assuming an obnoxious form. The fluorine, being apparently a constituent of the phosphate, cannot be removed by the miner, but, as pointed out by Dr. Wyatt, the greater part of the sand and clay can be got rid of by careful and systematic washing; and he also shows effectively the need and advantages of a proper chemical control of mining operations. The following figures, though but the results of laboratory experiments, may be of interest in this connection :

To observe the effect of a dry concentration, some "rock-phosphate" (No. 74, Florida collection) was crushed and passed through a 10-mesh sieve. The material was then sifted on a 20-mesh sieve, yielding A (coarser than 20-mesh) 64.62 per cent., B (finer) 35.38 per cent. B₂ was washed in a sort of *spitzkasten*, and gave:

| | Per cent. | Per cent. |
|------------------------------------|-----------|--------------------------------|
| B ₁ (coarsest), | 34.10 | or 12.06 of original material. |
| B ₂ (middle), | 15.00 | " 5.31 " " |
| B ₃ (finest), | 46.10 | " 16.31 " " |
| Loss in suspended matter, . . | 4.80 | " 1.70 " " |

In each portion the insoluble matter, phosphoric acid and the combined weight of the alumina and ferric oxide (equal to half the weight of the precipitated phosphates) were determined as follows, the phosphoric acid being given as such, and also calculated into its equivalent of calcium phosphate:

| | Total sample. | A | B | B ₁ | B ₂ | B ₃ |
|--|---------------|-------|-------|----------------|----------------|----------------|
| Insoluble, | 5.85 | .53 | 8.56 | .51 | 6.26 | 14.53 |
| Al ₂ Fe ₂ O ₃ , | 5.13 | 3.36 | 6.32 | 2.41 | 3.54 | 7.79 |
| P ₂ O ₅ , | 33.98 | 37.83 | 32.60 | 37.44 | 34.69 | 29.98 |
| Ca ₃ P ₂ O ₈ , | 74.20 | 82.38 | 71.18 | 81.70 | 75.75 | 65.63 |

Judging from the percentage of Al₂, Fe₂, O₃, we find that, by a simple mechanical process we have obtained in A, B₁, and B₂, high-grade phosphate amounting to 82 per cent. of the original sample, while B₃ contains too much of these oxides to be readily salable.

A more difficult problem is illustrated by the results of a similar

treatment of some of the "phosphatic sand-rock" of the Ichetucknee region in Florida. This is of low-grade in phosphoric acid, and contains much fine sand and clay; and a test was made to see if these impurities could be removed by the same operation as before. The sample yielded, in percentage, A, 20.74; B, 79.26; and B consisted of B₁, 37.83; B₂, 20.87; B₃, 17.75, and loss, 2.81. Analysis gave:

| | Total sample. | A | B | B ₁ | B ₂ | B ₃ |
|--|---------------|-------|-------|----------------|----------------|----------------|
| Insoluble, | | 34.77 | 18.13 | 44.19 | 62.55 | 38.11 |
| Al ₂ Fe ₂ O ₃ , | | 7.09 | 6.53 | 7.70 | 2.96 | 7.97 |
| P ₂ O ₅ , | | 24.08 | 30.49 | 20.36 | 13.75 | 25.02 |
| Ca ₃ P ₂ O ₈ , | | 52.49 | 65.46 | 43.38 | 29.97 | 54.54 |

Evidently, we have here a substance very different from the preceding one. The first is a metamorphosed rock; the second, the product of a sedimentation, by which the phosphate, sand and clay have been so intimately mixed that it will be difficult to devise a concentration-method which will furnish a phosphate suitable for the fertilizer-trade.

A third example is the "land-pebble," with its matrix, from the vicinity of Bartow, Florida. A sample disintegrated with water, without crushing, and thoroughly washed in a 20-mesh sieve, gave "pebble" 54.54, "matrix" 45.46 per cent. The analytical results of present interest are:

| | | Pebble. | Matrix. |
|--|-----------|---------|---------|
| Insoluble, | | 4.34 | 49.78 |
| Al ₂ Fe ₂ O ₃ , | | 4.05 | 9.38 |
| P ₂ O ₅ , | | 34.72 | 13.58 |
| Ca ₃ P ₂ O ₈ , | | 75.69 | 29.60 |

These figures show that simple washing on sieves, down to 20-mesh, is the best way to handle this material. Possibly, by washing the matrix further, on a 40-mesh sieve, a coarse product of some value might have been obtained; but the practical limit has probably been reached as above.

It would be easy for any one desiring to make such investigations to construct simple washing apparatus capable of treating large samples. The different grades of product should be dried and sampled, and the samples should be sent to a chemist for analysis. In many attempts to devise some simple apparatus for approximate determination of the phosphoric acid, at least, without special laboratory facilities, I have met with no success. The measurement of the volume of the yellow molybdate precipitate has been often proposed

as a means of rapid estimation of phosphoric acid; but numerous series of experiments, by myself and others, have shown that the information thus gained is but little more accurate than the estimate formed upon inspection by the practiced eye of the miner.

THE ANALYSIS OF A NATURAL PHOSPHATE.

The sample should be ground fine enough to leave no residue on an 80-mesh sieve, and should be thoroughly mixed by passing it three times through a 40-mesh sieve.

Moisture.—Two grammes are weighed into a tared platinum crucible. This, with its lid, is placed in an air-bath at 105° C., and heated for at least three hours. The lid is then put on, and the crucible is placed in a desiccator and weighed as soon as cold. The loss in weight is the moisture.

Combined Water and Organic Matter.—The residue from the moisture-determination is gradually heated to full redness over a Bunsen lamp, and then ignited over the blast-lamp. This operation is repeated after weighing until a constant weight is obtained. The loss (after deducting the percentage of carbonic acid as found in another portion) may be taken as water and organic matter. This method is sufficient for all practical purposes; but when minerals containing fluorine are strongly ignited, a part of the fluorine is expelled; hence, if more accurate determinations are required, the methods given in the standard works on analysis may be used.

Carbonic Acid.—Many forms of compact apparatus have been devised for this estimation, but none of them are satisfactory if accurate results are desired. Not to mention other objections, many phosphates must be heated nearly to boiling-point with dilute acid to effect complete decomposition of the carbonates. The distillation-method, described by Gooch (Bulletin No. 47, United States Geological Survey), is excellent, and when once the apparatus is set up, its work will be found to be rapid and satisfactory.

Insoluble Matter, Phosphoric Acid, Alumina, Ferric Oxide, Lime, and Magnesia.—Five grammes of the phosphate are put into a beaker; 25 c.c. nitric acid (specific gravity 1.20) and 12.5 c.c. hydrochloric acid (specific gravity 1.12) are added; and the beaker, covered with a watch glass, is placed upon the water-bath for thirty minutes. The contents of the beaker are well stirred from time to time, and at the end of the period the beaker is removed from the bath, filled with cold water, well stirred, and allowed to settle. The

solution is next filtered into a 500 c.c. flask, and the residue is thoroughly washed with cold water, partially dried, and then ignited (finishing with the blast-lamp) and brought to constant weight. The figures thus obtained will, however, be incorrect, because the fluorine liberated during the solution of the phosphate dissolves a portion of the silica. Hence, the results are too low. Nevertheless, as the same reaction would occur in the manufacture of a superphosphate from the material, the determination may be considered as a fair approximation to commercial practice. The ignited residue must be tested for P_2O_5 .

The flask containing the filtrate is filled up to the mark with cold water, and the solution is thoroughly mixed by twice pouring into a dry beaker and returning it to the flask. Cold water—not hot water, as recommended by Dr. Wyatt—is used for washing the residue, since if hot water is used, the sesquichlorides are apt to become basic and insoluble, and hence to remain in the residue and filter-paper. Besides, as the flask is to be filled to the mark, the contents must be cold before any volumetric measurements can be made.

Phosphoric Acid.—Two portions of the solution, 50 c.c. each = .5000 gramme of original material, are put into beakers and evaporated until all the hydrochloric acid is driven off. (Although it is asserted that a moderate amount of this acid does not interfere with this determination, I prefer to be sure of its absence.) Then 150 c.c. of molybdate solution are added to each portion, which is well stirred and allowed to stand on the water-bath until quite hot; then removed and allowed to stand until perfectly cold. It is best to let it stand for at least three hours, after which the yellow precipitate is filtered and well washed with a 20 per cent. solution of ammonium nitrate, containing $\frac{1}{30}$ of its volume of nitric acid (which I prefer to use, although the precipitate is considered, on good authority, to be insoluble in cold water). The filtrate should be tested for any remaining P_2O_5 by adding some molybdate solution and digesting it for some time. The funnel, with its contents, is now inclined over the beaker in which the precipitation was effected, and the precipitate is washed back into it with a jet of pure water. Ammonia water in slight excess is then added, and on gently warming the beaker complete solution should take place. Any residue indicates either incomplete washing or, under some circumstances, silica. The solution is filtered through the same filter into a clean beaker, and the first beaker and the filter are washed with ammonia wash-water (1 part strong ammonia to 4 parts water). The filtrate is now brought

to a boil and removed from the lamp, and magnesia solution is added, drop by drop, with continual stirring. The precipitate at first redissolves, but during the continued addition of the magnesia the solution becomes cloudy with a flocculent precipitate, which, however, as the stirring is continued, becomes crystalline and subsides rapidly. When further addition of the precipitant causes no cloudiness, and the crystalline change is complete (which is most important), the beaker is placed in very cold water to chill its contents as rapidly as possible. When perfectly cold, it is again tested with a drop of magnesia solution, and, if the precipitation is found to be complete, about one-third of its volume of strong ammonia is added, the whole stirred and allowed to stand at least three hours (although I have had perfectly good results after the lapse of not more than one hour).

The precipitate is finally filtered on an asbestos felt* in a Gooch perforated crucible, and washed with the 1 : 3 ammonia-water. As the removal of the precipitate from the sides of the beaker requires much rubbing and much wash-water, the washing will be complete as soon as the beaker is clean. Two or three drops of a strong solution of ammonium nitrate are poured on the precipitate, which is then carefully dried and gently heated until the fumes of ammonium salts ceases to come off. The heat is then increased, and as soon as the glow of the pyrophosphate formation has passed through the whole of the precipitate, the crucible is placed in a desiccator and, when cold, weighed. The ignited precipitate is very white, and the difference between the two determinations of P_2O_5 ought not to exceed .05 per cent. for thoroughly satisfactory work, although, as shown in the column of analytical results at the end of this paper, it sometimes exceeds this limit, since, as but one half-gramme is used for each determination, any error is doubled in the final calculation.

In default of a Gooch crucible, the ammonium-magnesium-phosphate should be filtered on paper, and, after washing, dissolved in dilute nitric acid, evaporated in a platinum crucible to complete dryness, carefully ignited and weighed. A clean mass is thus obtained, while, on the other hand, if the precipitate be ignited with the paper, it is difficult to destroy the carbon.

Lime, Alumina and Ferric Oxide.—The Glaser method for alumina and ferric oxide was used in the earlier part of the work here de-

* Gooch, *Am. Chem. Jour.*, vol. i., p. 317.

scribed, but later the method as improved by R. Jones (*Zeitschrift f. Angew. Chemie*, 1891, Heft I.) was adopted and has been found entirely satisfactory. As I use it, the process is as follows:

Lime.—One hundred centimeters of the solution (containing 1 gramme of the original substance) are evaporated in a beaker to about 50 c.c.; 10 c.c. of dilute sulphuric acid (1 c.c. H_2SO_4 diluted to 5) are added; and the evaporation is continued on the water-bath until a considerable crop of crystals of gypsum has formed. The solution is then allowed to cool, when it generally becomes pasty, owing to the separation of additional gypsum. When it is cold, 150 c.c. of 95 per cent. alcohol are slowly added, with continual stirring, and the whole is allowed to stand for three hours, being stirred from time to time. After three hours it is filtered, with the aid of a filter-pump, into a distillation-flask, and the beautifully crystalline precipitate, which does not adhere to the beaker, is washed with 95 per cent. alcohol. The filter, with the precipitate, is gently removed from the funnel and inverted into a platinum crucible, so that, by squeezing the point of the filter, the precipitate is made to fall into the crucible, and the paper can be pressed down smoothly upon it. On gentle heating of the crucible, the remaining alcohol burns off, and when the paper has been completely destroyed, the heat is raised to the full power of a Bunsen lamp for about five minutes, after which the crucible can be cooled and weighed. The precipitate is then $CaSO_4$, and the results are very close, a pair of determinations of CaO (calculated from the $CaSO_4$) rarely differing more than .05 per cent., as will be seen below.

Alumina and Ferric Oxide.—The distillation-flask containing the alcoholic filtrate is connected with its condenser and heated on a water-bath until no more alcohol comes over. This distillate, if mixed with a little sodium carbonate and redistilled over quicklime, can be used over and over again, so that the expense for alcohol is really very slight, while in the use of the Glaser method, with its large amount of sulphuric acid, all the alcohol is lost.

When the distillation is ended, the residue in the flask is washed into a small platinum dish and evaporated as far as possible on the water-bath. It will become dark-brown, owing to the presence of organic matter, which must be destroyed, since it prevents the complete precipitation of the phosphate in the subsequent operation. This destruction of the organic matter is best affected, according to my experience, by removing the dish from the bath, adding a small quantity of pure sodium nitrate and heating very carefully over the

naked flame, while keeping the dish well covered with a watch-glass. If care be taken, there will be no loss by spattering; and the mass fuses to a colorless, viscous liquid, cooling to a glass, which is readily soluble in hot water made acid with nitric acid.

The solution is transferred to a beaker, made slightly (but distinctly) alkaline with ammonia; then carefully neutralized with acetic acid; then diluted with hot water, brought to the boil, allowed to settle and filtered. After the precipitate, which does not adhere to the beaker, has been completely brought upon the filter by means of hot water, the washing is completed with a solution of ammonium nitrate (made by neutralizing 5 c.c. HNO_3 with ammonia and diluting to 250 c.c.), and the precipitate is dried, ignited at full lamp-heat, cooled and weighed. As the determinations are made in pairs, one portion is used for the estimation of the phosphoric acid by fusing it with a little sodium carbonate, dissolving in dilute nitric acid and treating with molybdate solution as already described, while the other portion, also fused with sodium carbonate, is dissolved with sulphuric acid, and the iron is reduced and titrated with permanganate.

The average of the results by this method will show that the weights of the two portions of the aluminum ferric phosphate (usually symbolized alfe) should not differ more than 1 milligramme, which, upon the conventional division by 2, gives a difference of .05 per cent. for the combined oxides; but, in general work, if the results for the combined oxides do not vary more than one-tenth of 1 per cent., the method ought to be considered very satisfactory, since it is easy to execute, and requires but little time in actual labor.

Magnesia.—The filtrate from the alfe is evaporated to a small bulk, made strongly ammoniacal, and allowed to stand; when magnesia, if present, will separate as the double salt, and should be treated as usual. If, during the evaporation of the filtrate (which should be perfectly clear at first) any flocculent matter separates, this should be filtered off and examined before precipitating the magnesia.

Fluorine.—Two grammes of the phosphate are intimately mixed in a large platinum crucible with 3 grammes of precipitated silica and 12 grammes of pure sodium carbonate, and the mixture is gradually brought to clear fusion over the blast-lamp. When the fusion is complete, the melt is spread over the walls of the crucible, which is then rapidly cooled (preferably by the blast of air). If this has been properly done, the mass separates easily from the crucible, and the

subsequent leaching is hastened. The mass, detached from the crucible, is put into a platinum dish, into which whatever remains adhering to the crucible, or its lid, is also washed with hot water. A reasonable amount of hot water is now put into the dish, which is covered and digested on the water-bath until the mass is thoroughly disintegrated. To hasten this, the supernatant liquid may after awhile be poured off, the residue being washed into a small porcelain mortar, ground up, returned to the dish and boiled with fresh water until no hard grains are left. The total liquid is then filtered, and the residue is washed with hot water. The filtrate (which should amount to about 500 c.c.) is nearly neutralized with nitric acid (methyl orange being used as indicator), some pure sodium bicarbonate is at once added, and the solution (in a platinum dish, if one large enough is at disposal, otherwise in a beaker), is placed on the water-bath, when it speedily becomes turbid through separation of silica. As soon as the solution is warm it is removed from the bath, stirred, allowed to stand for two or three hours, and then filtered by means of the filter-pump and cold wash-water.

The filtrate is concentrated to about 250 c.c., and nearly neutralized, as before; some sodium carbonate is added; and the phosphoric acid is precipitated with silver nitrate in excess. The precipitate is filtered off and washed with hot water, and the excess of silver in the filtrate is removed with sodium chloride. The filtrate from the silver chloride (after addition of some sodium bicarbonate) is evaporated to its crystallizing point, then cooled and diluted with cold water; still more sodium bicarbonate is added, and the whole is allowed to stand, when additional silica will separate and is to be filtered off.

This final solution is nearly neutralized, as before; a little sodium carbonate solution is added; it is heated to boiling, and an excess of solution of calcium chloride is added. The precipitate of calcium fluoride and carbonate must be boiled for a few minutes, when it can be easily filtered and washed with hot water. The washed precipitate is then washed from the filter into a small platinum dish and evaporated to dryness, while the filter, after being partially dried and used to wipe off any particles of the precipitate adhering to the dish in which it was formed, is burned, and the ash is added to the main precipitate. This, when dry, is ignited, and allowed to cool; dilute acetic acid is added in excess, and the whole is evaporated to dryness, being kept on the water-bath until all odor of acetic acid has disappeared. The residue is then treated with hot water, di-

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gested, filtered on a small filter, washed with hot water, partially dried, put into a crucible, carefully ignited and weighed as CaF_2 . The CaF_2 is then dissolved in H_2SO_4 by gentle heating and agitation, evaporated to dryness on a radiator, ignited at full red heat and weighed as CaSO_4 . From this weight the equivalent weight of CaF_2 should be calculated, and should be very close to that actually found as above, but should never exceed it. The difference, which is generally about a milligramme (sometimes more), is due to silica precipitated with the fluoride. The percentage of fluorine is, therefore, always calculated from the weight of the sulphate, and not from that of the original fluoride.

The main improvements in this method are the use of sodium bicarbonate to separate the silica, and the keeping of the earlier solutions as dilute as possible, which cannot be done if ammonium carbonate is used for the separation of the silica. These changes make the fluorine estimation, although still tedious, far more rapid than before, and the results are very satisfactory.

The following are the results obtained by these methods in the analysis of the last twelve samples examined. In these cases the methods, as given above, have been followed in all their details, and the figures are fairly representative :

| Sample No. | $\frac{\text{Alfe}}{2}$ Per cent. | CaO Per cent. | P_2O_5 Per cent. | F1. Per cent. |
|------------|--------------------------------------|------------------|-------------------------------------|------------------|
| 55 | 2.30-2.28 | 50.99-50.63 | 35.37-35.33 | 2.66-..... |
| 111 | 4.20-4.19 | 47.04-46.99 | 33.91-33.90 | 2.35-2.24 |
| 99 | 2.50-2.62 | 52.01-52.02 | 38.78-38.79 |-..... |
| 96 | 4.23-4.22 | 50.09-50.07 | 38.82-38.86 | 2.46-2.45 |
| 98 | 7.93-7.79 | 44.04-44.05 | 35.28-35.10 | 2.55-2.59 |
| 1 | 2.54-2.49 | 33.10-33.03 | 21.05-21.06 | 3.17-..... |
| 63 | .46-.48 | 54.46-54.42 | 37.70-37.77 | 3.08-3.00 |
| 940 | 3.15-3.19 | 46.06-46.00 | 31.49-31.51 | 1.87-1.86 |
| 950 | 2.20-2.16 | 45.69-45.68 | 28.49-28.45 | 2.45-2.54 |
| 947 | 3.47-3.55 | 42.74-42.81 | 28.33-28.38 | 2.48-2.41 |
| 937A | 4.05-4.06 | 47.96-47.94 | 34.77-34.67 | 2.72-2.73 |
| 937B | 9.39-9.37 | 15.95-15.89 | 13.55-13.61 | .88-..... |

